ISSN 1070-4280, Russian Journal of Organic Chemistry, 2018, Vol. 54, No. 1, pp. 149–150. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.G. Khusainova, V.A. Burilov, D.I. Samigullin, 2018, published in Zhurnal Organicheskoi Khimii, 2018, Vol. 54, No. 1, pp. 147–148.

SHORT COMMUNICATIONS

Reaction of Diethyl Vinylphosphonate with Benzimidazole and 2-Aminobenzimidazole

N. G. Khusainova,* V. A. Burilov, and D. I. Samigullin

Kazan Federal University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia
**e-mail: narkis.khusainova@kpfu.ru*

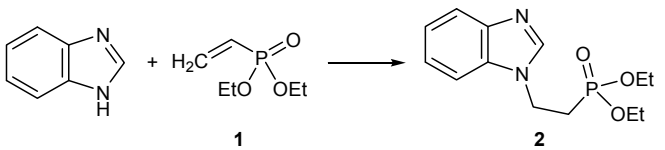
Received March 1, 2017

Abstract—Benzimidazole reacted with diethyl vinylphosphonate to give diethyl 2-(1*H*-benzimidazol-1-yl)-ethylphosphonate. The addition of 2-aminobenzimidazole to vinylphosphonate involved the endocyclic nitrogen atom with formation of diethyl 2-(2-imino-2,3-dihydro-1*H*-benzimidazol-1-yl)ethylphosphonate.

DOI: 10.1134/S1070428018010177

Benzimidazole derivatives show diverse biological activities; many known drugs, in particular hypotensive, vasodilating, spasmolytic (bendazole), antisecretory (omeprazole, rabeprazole), antihelminthic (mebendazole, albendazole), and atntitumor agents, have been developed on their basis [1]. With the goal of obtaining new potentially practically important compounds containing a pharmacophoric benzimidazole fragment, in this work we studied the reactions of diethyl vinylphosphonate (**1**) with benzimidazole and 2-aminobenzimidazole. By heating an equimolar mixture of phosphonate **1** and benzimidazole we obtained an oily product (**2**) whose ^{31}P NMR spectrum showed only one signal at δ_P 26.1 ppm, indicating the formation of a single adduct. In the ^{1}H NMR spectrum of **2** we observed a doublet of triplets at δ 2.32 ppm with a coupling constant $^2J_{PH}$ of 18.5 Hz typical of methylene protons in the α-position with respect to the phosphorus atom. These findings suggest addition of the nitrogen atom of benzimidazole to the β-carbon atom of vinylphosphonate **1**. The electron impact mass spectrum of **2** contained a ion peak with *m*/*z* 282 corresponding to the formation of 1:1 adduct. Among fragment ion peaks, the most intense was that with *m*/*z* 145, which was identified as 1-ethyl-1*H*-benzimidazole ($C_9H_{10}N_2$) resulting from thermal decomposition of compound **2** via elimination of the phosphoryl group. On the basis of the ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra, the product was assigned the structure of diethyl 2-(1*H*-benzimidazol-1-yl)ethylphosphonate (**2**) (Scheme 1).

Scheme 1.



1 **2**

Theoretically, the reaction of vinylphosphonate with 2-aminobenzimidazole can involve both endocyclic nitrogen atom (path *a*) and nitrogen atom of the exocyclic amino group (path *b*). Phosphonate **1** reacted with 2-aminobenzimidazole on heating at 70–75°C for 20 h to give compound **3** which was isolated as a powder-like material. The mass spectrum of **3** displayed a ion peak with *m*/*z* 297, indicating addition of only one 2-aminobenzimdazole molecule to vinylphosphonate **1**.

Consideration of possible product structures shows that, unlike unsymmetrical structure **3**, the imidazole fragment in **4** is symmetrical due to tautomerization via proton transfer from one endocyclic nitrogen atom to the other. Therefore, the ^{13}C NMR spectrum of **4** was expected to display similar chemical shifts of carbon atoms in positions *4* and *7*, as well as in positions *5* and *6*. In the spectrum of unsymmetrical compound **3**, signals from all carbon atoms in the imidazole fragment should be different. In fact, all carbon signals appeared separately in the ^{13}C NMR spectrum of the isolated compound. Therefore, we presumed that the reaction of phosphonate **1** with 2-aminobenzimidazole involved the endocyclic nitrogen atom of the latter. The ^{1}H and ^{31}P NMR spectra